Anomalous superconducting-gap symmetry of noncentrosymmetric La_2C_3 observed by ultrahigh-resolution photoemission spectroscopy

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We have performed ultrahigh-resolution photoemission spectroscopy on noncentrosymmetric superconductor La_2C_3 to study the electronic structure near the Fermi level (E_F) and the superconducting-gap symmetry. We clearly observed the opening of the superconducting gap, as evidenced by the emergence of a sharp quasiparticle peak just below E_F together with the leading-edge shift toward higher binding energy. Quantitative analysis of the gap function has revealed a marked deviation from the single *s*- or *d*-wave symmetry, suggesting the existence of multiple superconducting gaps.

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The discovery of superconductivity in a noncentrosymmetric heavy-fermion compound $CePt_3Si$ has provoked much attention on the electronic structure and its relation to the mechanism of superconductivity.[1] In particular, a hot debate has arisen on the pairing symmetry of this class of superconductors that lack the inversion symmetry in the crystal structure.[2] It is well known that the spin degeneracy of energy bands is lifted in a noncentrosymmetric crystal due to the antisymmetric spin-orbit coupling, and the broken space-inversion symmetry would violate the standard classification of Cooper pairs in terms of even or odd parity (spin singlet or triplet), leading to a peculiar pairing state where the spin singlet and triplet states are indistinguishably mixed.[2] The spin-lattice relaxation rate of $CePt_3Si$ shows a coherence peak suggestive of the isotropic energy gap, while it shows a distinct deviation from the power-law behavior at low temperatures, indicating the presence of a line node.[3] The magnetic penetration depth[4] and the thermodynamic transport measurements[5] are in favor of the latter case. Although both Li_2Pd_3B and Li_2Pt_3B are noncentrosymmetric superconductors with the identical crystal structure,[6,7] the multiple-[8] or *s*-wave-gap symmetry[9] has been proposed for Li_2Pd_3B, while the anisotropic-gap symmetry with a line node[8] has been suggested for Li_2Pt_3B. It is, thus, not well understood even experimentally whether the noncentrosymmetric superconductor possess a common unusual pairing symmetry, and if it is the case, what type of superconducting-gap symmetry it has.

Recently, the superconductivity has been discovered also in metallic carbides R_2C_3 (R=Y and La),[10,11] which crystallize in the cubic Pu_2C_3-type structure with no inversion center. This compound could serve as an ideal candidate to investigate the pairing symmetry of noncentrosymmetric superconductors without the influence from the strong electron correlation and/or the magnetic fluctuation. Unconventional superconductivity such as the multiband superconductivity[12,13] or the mixture of *s*- and *p*-wave symmetries[2] would be regarded as a possible superconducting order parameter. However, the validity of these models as well as the possibility of other pairing channels have not been well examined yet, mainly because of the lack of experimental input on the electronic structure near the Fermi level (E_F), in particular, on the low-energy excitations relevant to superconductivity.

In this Brief Report, we report results of ultrahigh-resolution photoemission spectroscopy on noncentrosymmetric La_2C_3 single crystal. By using the ultrahigh resolution (ΔE=1.7 meV), we have observed the opening of the superconducting gap at low temperatures. We found that the spectral line shape showing the superconducting gap is substantially deviated from that of the simple single-component *s*- or *d*-wave symmetry, but is reasonably explained by the presence of two-component energy gaps with significantly different coupling parameters.

High-quality single crystals of La_2C_3 were grown by the self-flux method. The sharp x-ray diffraction pattern shows the high quality without inclusion from other phases, and the magnetization measurement has confirmed the occurrence of superconductivity with the superconducting transition temperature (T_c) of 6.5 K. Ultrahigh-resolution photoemission measurements were performed using a Scienta SES2002 spectrometer with a high-flux discharge lamp and a toroidal grating monochromator at Tohoku University. The He Iα ($h\nu$=21.218 eV) and He IIα (40.814 eV) resonance lines were used to excite photoelectrons. The energy resolution (ΔE) was set at 1.7 meV, except for the measurement of the wide valence-band region (ΔE=4 meV). Crystals were fractured *in situ* in an ultrahigh vacuum of 2×10^{-11} Torr to obtain a clean surface for the measurements. We have confirmed that the degradation of sample surface did not take place during the measurements, and the data shown here are reproducible by measuring several different samples. We have also confirmed that the obtained photo emission spectroscopy (PES) spectra show no discernible angular dependence, indicating that the PES spectra are well angle integrated. The Fermi level (E_F) of samples was referred to that of a gold film evaporated onto the sample substrate.

Figure 1 shows the valence-band photoemission spectra of La_2C_3 measured at 4.5 K with the He Iα and He IIα resonance lines. We find three prominent peaks located at 1, 4, and 7 eV, respectively, in both He I and He II spectra, while the relative intensity of these peaks are slightly different between the He I and He II spectra, possibly due to the cross-section effect. We also find that the He II spectrum shows an

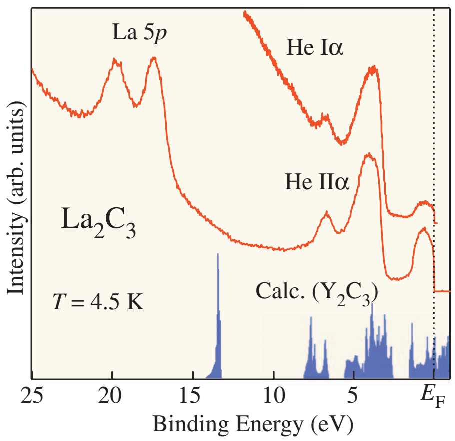

FIG. 1. (Color) Angle-integrated photoemission spectra of La_2C_3 measured at 4.5 K with He Iα and He IIα resonance lines. Calculated density of states of Y_2C_3 (Ref. 14) is also shown for comparison.

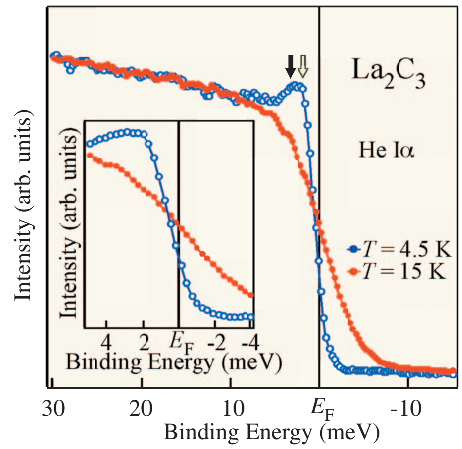

FIG. 2. (Color) Ultrahigh-resolution angle-integrated photoemission spectra near E_F measured at 4.5 K (blue open circles) and 15 K (red filled circles) with He Iα resonance line. Inset shows the expansion in the vicinity of E_F. Open and filled arrows on the 4.5 K spectrum denote the approximate energy position of the first and second peaks, respectively.

additional large doublet structure around 19 eV. This doublet structure is not seen in the He I spectrum because of the lower excitation energy in the He I measurement. We also show in Fig. 1 the electron density of states (DOS) of Y_2C_3 calculated by the scalar relativistic self-consistent full-potential linear muffin-tin method within the local density approximation (LDA).[14] Since the calculation for La_2C_3 is not available at present, we compare the present photoemission result with the calculation for Y_2C_3 by taking account of the possible difference between the 4*d* (Y) and 5*d* (La) states. As seen in Fig. 1, the DOS calculated for Y_2C_3 tracks well the energy position of experimentally obtained valence bands of La_2C_3, suggesting that the valence band consists of essentially the C 2*p* states and/or the difference between the Y 4*d* and La 5*d* states is just a small contribution to the valence band. According to the calculation,[14] the bunch of calculated DOS located at E_F and 4 eV is mainly due to the hybridized states of the Y 4*d* and C 2*p* orbitals, while the prominent DOS around 7 eV originates mainly from the C 2*s* orbital hybridized with Y 4*d* states. The sharp calculated DOS around 14 eV is mainly due to the C 2*s* states. It is noted here that another LDA calculation by Singh and Mazin[15] reported a similar result, with a small quantitative difference in the width and the position of the bands. We therefore assign the two bands in La_2C_3 observed by photoemission at 1 and 4 eV to the La 5*d* and C 2*p* hybridized states, and the small peak at 7 eV to the La 5*d* and C 2*s* hybridized states. The broad shoulderlike structure around 15 eV in the experiment may correspond to the DOS at 14 eV in the calculation, although the weight is considerably small in the experiment. A large doublet structure around 19 eV in the He II spectrum is assigned to the spin-split La 5*p* core level.[16] It is noted that the band calculation of Y_2C_3 does not show such a doublet structure simply because the calculation does not include the Y 4*p* states.

Figure 2 shows ultrahigh-resolution photoemission spectra in the vicinity of E_F of La_2C_3 measured with the He Iα resonance line at temperatures (4.5 and 15 K) below and/or above the T_c (6.5 K). The spectral intensity is normalized to the area under the curve. As seen in Fig. 2, the spectrum clearly shows a remarkable temperature dependence that is not accounted for by the simple temperature effect due to the Fermi-Dirac (FD) distribution function. The midpoint of the leading edge in the spectrum at 4.5 K is not at E_F, but is shifted by about 0.6 meV toward the high binding energy with respect to E_F (see the inset of Fig. 2). In contrast, the spectrum at 15 K has the leading-edge midpoint at E_F. It is remarked that the 4.5-K spectrum exhibits a small but distinct quasiparticle peak at about 2 meV, while it totally disappears in the 15-K spectrum. This temperature-induced spectral change certainly indicates the opening and/or closing of a superconducting gap as a function of temperature in La_2C_3. A closer look at Fig. 2 further reveals an anomalous feature of the quasiparticle peak, which is apparently broad and rounded in comparison with the sharp quasiparticle peak observed by ultrahigh-resolution photoemission in conventional superconductors such as Nb (Ref. 17) and V_3Si.[18] The broad and rounded feature of the quasiparticle peak of La_2C_3 is hardly accounted for with a single peak, suggesting that the quasiparticle peak consists of two components (peaks), indicated by arrows in Fig. 2. This behavior is obviously different from the conventional superconductors which well follow the weak-coupling BCS spectral function with a single gap, but rather shows a close resemblance to the spectral behavior of the two-gap superconductor MgB_2.[19,20]

In order to examine the conjecture described above as well as to reveal the symmetry and the size of the superconducting gap(s), we have performed numerical fittings to the photoemission spectrum and shown the results in Fig. 3. At first, we examined the single-gap scenario by using the single *s*-wave or *d*-wave Dynes function $N(\omega,\Delta,\Gamma)$ with the parameters of ω, Δ, and Γ, where ω, Δ, and Γ are the energy relative to E_F, the size of the superconducting gap, and the phenomenological broadening factor, respectively.[21] In the case of *d*-wave gap, we assumed a cylindrical Fermi surface. The Dynes function for each gap symmetry is multiplied by the FD function at 4.5 K, and then convoluted with a Gauss-

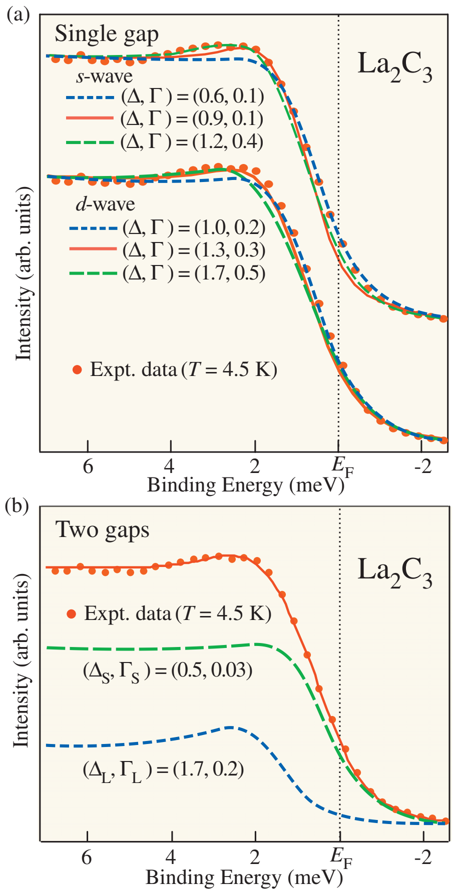

FIG. 3. (Color) (a) Representative fitting curves to the 4.5 K spectrum (red dots) by using the single *s*- or *d*-wave Dynes function with three different parameter sets. (b) Fitting result (red solid curve) of the 4.5 K spectrum with the two-component Dynes function. Green long-dash and blue short-dash curves show the fitting curves for the small and large gaps, respectively. The size of superconducting gap (Δ) and the broadening factor (Γ) are in units of meV.

ian with a full width at half maximum of 1.7 meV to incorporate the instrumental resolution. Although we have tried many fittings within a reasonable parameter space of the gap size and the broadening factor, the experimental spectrum at 4.5 K is hardly reproduced in both cases as shown in Fig. 3(a), where we see that the quasiparticle-peak position and the leading edge are not well reproduced simultaneously within the single-gap scheme. These results suggest that the gap function beyond the single *s*- or *d*-wave symmetry should be taken into account to explain the anomalous superconducting gap of La_2C_3. As an alternative candidate of the gap function, we assumed the presence of two isotropic *s*-wave gaps, whose gap function is described as $\alpha N(\omega,\Delta_S,\Gamma_S)+(1-\alpha)N(\omega,\Delta_L,\Gamma_L)$, where α is the ratio between the two gaps, and S and L denote small and large gaps, respectively. As shown in Fig. 3(b), the fitting curve with a small gap of Δ_S=0.5 meV and a large gap of Δ_L=1.7 meV at α=0.7 reproduces the photoemission spectrum very well, both in the shape of the quasiparticle peak and the position and/or slope of the leading edge. By assuming the BCS-like temperature dependence, we have estimated the gap size at 0 K to be 0.6 and 2.1 meV for the small gap and the large gap, respectively, which correspond to $2\Delta(0)/k_BT_c$=2.1 and 7.2. This indicates that the large gap has the coupling constant in the strong-coupling regime, while that of the small gap is well below the weak-coupling BCS value (3.53). It is worthwhile to note that the well-established two-gap superconductor MgB_2 also shows the coexistence of the strong- and weak-coupling gaps with $2\Delta/k_BT_c$=4 and 1.[19,20] A recent ^{13}C NMR experiment on Y_2C_3 reported a characteristic kink of $1/T_1T$ around 3 K, greatly below T_c (15.7 K),[13] which is well explained by the presence of two gaps with $2\Delta/k_BT_c$=5 and 2, consistent with the present photoemission result. The existence of a line node due to the singlet-triplet mixing and/or the anisotropic *s*-wave gap may be unlikely in La_2C_3, because the fairly small broadening factor observed for the small gap (Γ_S=0.03 meV) suggests the nearly isotropic nature of the *s*-wave gap. All these experimental results support the existence of two superconducting gaps with the *s*-wave symmetry. Recently, the two-band effect on the superconductivity has been theoretically discussed for Th-doped Y_2C_3 and La_2C_3.[12] The theory predicts that although the spin-orbit coupling lifts the spin degeneracy of bands in most of the Brillouin zone, the spin-split Fermi surfaces touch each other along certain directions in the Brillouin zone due to the high crystallographic symmetry, producing the multiband effects in the superconducting state, where the superconducting gap would have multiple components. In order to examine the proposed two-band effect and reveal the origin of the anomalous superconductivity in La_2C_3, it is strongly desired to perform angle-resolved photoemission spectroscopy to directly observe the momentum dependence of the superconducting gaps.

In summary, we have reported ultrahigh-resolution photoemission spectroscopy on noncentrosymmetric superconductor La_2C_3. The photoemission spectrum at the superconducting state clearly shows a quasiparticle peak just below E_F, indicative of the superconducting-gap opening. The quasiparticle peak is broad and rounded compared to that of conventional superconductors. The numerical fittings have revealed that the spectrum is hardly reproduced with a single *s*- or *d*-wave gap, but is satisfactorily explained by two gaps with the gap values of 0.5 and 1.7 meV, respectively. All these experimental results suggest that La_2C_3 is a two-gap superconductor.

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[1] E. Bauer, G. Hilscher, H. Michor, Ch. Paul, E. W. Scheidt, A. Gribanov, Yu. Seropegin, H. Noël, M. Sigrist, and P. Rogl, Phys. Rev. Lett. **92**, 027003 (2004).
[2] N. Hayashi, K. Wakabayashi, P. A. Frigeri, and M. Sigrist, Phys. Rev. B **73**, 092508 (2006).
[3] M. Yogi, Y. Kitaoka, S. Hashimoto, T. Yasuda, R. Settai, T. D. Matsuda, Y. Haga, Y. Onuki, P. Rogl, and E. Bauer, Phys. Rev. Lett. **93**, 027003 (2004).
[4] I. Bonalde, W. Brämer-Escamilla, and E. Bauer, Phys. Rev. Lett. **94**, 207002 (2005).
[5] K. Izawa, Y. Kasahara, Y. Matsuda, K. Behnia, T. Yasuda, R. Settai, and Y. Onuki, Phys. Rev. Lett. **94**, 197002 (2005).
[6] K. Togano, P. Badica, Y. Nakamori, S. Orimo, H. Takeya, and K. Hirata, Phys. Rev. Lett. **93**, 247004 (2004).
[7] P. Badica, T. Kondo, and K. Tagano, J. Phys. Soc. Jpn. **74**, 1014 (2005).
[8] H. Q. Yuan, D. Vandervelde, M. B. Salamon, P. Badica, and K. Tagano, Low Temp. Phys. **850**, 633 (2006).
[9] H. Takeya, K. Hirata, K. Yamaura, K. Togano, M. El Massalami, R. Rapp, F. A. Chaves, and B. Ouladdiaf, Phys. Rev. B **72**, 104506 (2005).
[10] G. Amano, S. Akutagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, J. Phys. Soc. Jpn. **73**, 530 (2004).
[11] A. Simon and T. Gulden, Z. Anorg. Allg. Chem. **630**, 2191 (2004).
[12] I. A. Sergienko, Physica B **359**, 581 (2005).
[13] A. Harada, S. Akutagawa, Y. Miyamichi, H. Mukuda, Y. Kitaoka, and J. Akimitsu, J. Phys. Soc. Jpn. **76**, 023704 (2007).
[14] I. R. Shein and A. L. Ivanovskii, Solid State Commun. **131**, 223 (2004).
[15] D. J. Singh and I. I. Mazin, Phys. Rev. B **70**, 052504 (2004).
[16] S. Hüfner, *Photoelectron Spectroscopy*, Springer Series in Solid State Sciences Vol. 82 (Springer-Verlag, Berlin, Heidelberg, 1995).
[17] A. Chainani, T. Yokoya, T. Kiss, and S. Shin, Phys. Rev. Lett. **85**, 1966 (2000).
[18] F. Reinert, G. Nicolay, B. Eltner, D. Ehm, S. Schmidt, S. Hüfner, U. Probst, and E. Bucher, Phys. Rev. Lett. **85**, 3930 (2000).
[19] S. Tsuda, T. Yokoya, T. Kiss, Y. Takano, K. Togano, H. Kito, H. Ihara, and S. Shin, Phys. Rev. Lett. **87**, 177006 (2001).
[20] S. Souma, Y. Machida, T. Sato, T. Takahashi, H. Matsui, S. C. Wang, H. Ding, A. Kaminski, J. C. Campuzano, S. Sasaki, and K. Kadowaki, Nature (London) **423**, 65 (2003).
[21] R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. **41**, 1509 (1978).